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Impurity States Associated with Subsidiary Energy-Band Minima*

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Abstract

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Two results have been established concerning the existence of localized electronic states associated with a point impurity in a substance having a spherical energy band, $E(k) = \epsilon_0 + \epsilon_1 \times \cos k + \epsilon_2 \cos 2k$, where $k = k$, with a subsidiary minimum at $k = 0$. The 1st result is a generalization of Slater and Koster's result, that in 1 dimension an energy band with a subsidiary minimum has no localized states associated with this minimum if the impurity potential is of the δ -function type; i.e., it has only 1 matrix element between Wannier functions, a diagonal one referring to 1 site. We show that this result also holds for a spherical band in 3 dimensions. Our 2nd result is that, for the Coulomb-impurity potential screened by the static dielectric constant, and the above spherical band, there are hydrogen-like localized states built out of states near the subsidiary minimum, even when all powers of k in $E(k)$ are taken into account in the equation for the envelope function. The deviation of the impurity potential from

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slow variation causes a long lifetime for decay of the localized state into conduction states of the same energy. For a typical shallow impurity state, the lifetime is $\approx 10^{-8}$ -- 10^{-9} sec.

Recently the existence of discrete localized electronic states, arising because of a localized impurity, and coincident in energy with states in an energy band has been invoked in order to explain a number of observations in semiconductors.¹ These states are of two slightly different types.

The first type is associated with the valence band systems in silicon and germanium. Spin-orbit coupling causes a partial breakdown of what would otherwise be a sixfold degeneracy at $\underline{k} = 0$ into two- and four-fold degeneracies, the fourfold degenerate band having the higher energy. If the perturbation potential caused by a localized impurity such as a type III or type V substitutional atom is sufficiently weak (i.e. its matrix elements are not comparable in size to the spin-orbit splitting at $\underline{k} = 0$), and it varies slowly over distances of unit cell dimensions, so that effective mass theory holds, one can imagine that the two-fold and the four-fold degenerate bands separately give rise to hydrogen-like localized states. In this case a localized state arising from the two-fold degenerate band will have the same energy as some continuum state of the four-fold degenerate band.

A second, similar situation arises when one considers the conduction band of germanium, which has four absolute minima at the ends of the $[1,1,1]$ axes in the Brillouin zone, and a subsidiary minimum at $\underline{k} = 0$. As above, one may suspect that localized states arise composed of Bloch states with \underline{k} vectors near the subsidiary minimum, in addition to the localized states that arise from Bloch states near the absolute minima. The weak point in such speculations is that the usual effective mass theory, upon which they are based (a form of perturbation theory) ignores the existence of possible continuum states degenerate with the localized

state that is created. Although a slowly varying potential has very small matrix elements between states with widely different k values, a small or vanishing unperturbed energy difference between these states may cause appreciable mixings of these types of unperturbed states in any state describing the perturbed system. As an example of such mixing we may mention that for a strongly localized impurity potential perturbing a monatomic one-dimensional solid having an energy band with a subsidiary minimum, Slater and Koster² have shown that no completely localized state exists associated with the subsidiary minimum regardless of the strength of the localized impurity potential. The purpose of this paper is to show that if certain restrictions of the effective mass approximation are removed, allowing one to effectively include interactions of all Bloch waves in an energy band, and if, in addition, the effective potential caused by the localized impurity is still slowly varying, rigorously localized states exist associated with a subsidiary minimum of the band. The remainder of the perturbation potential is estimated to be responsible for a lifetime long compared to a typical lifetime caused by the electron lattice interaction.

Let us first review some aspects of Slater and Koster's one-dimensional calculation. They consider an infinite one-dimensional monatomic crystal which contains a localized impurity. The wave function $\psi(x)$ for the perturbed problem is expanded as a linear combination of Wannier function $\phi_n(x - pa)$ for the different bands defined by the unperturbed, periodic Hamiltonian. Thus, $\psi(x) = \sum_{p,n} U_n(p) \phi_n(x - pa)$ where p is an integer, n is the band index, and a is the lattice spacing. The sum over p extends from $-\infty$ to $+\infty$. The simple case is treated in which the bands are decoupled, i.e. the impurity potential energy has no interband matrix

element between Wannier functions, and further, for any one band only one matrix element of the perturbation is non-zero: $\int \phi(x-pa) V(x) \phi(x-pa) dx = V_{00} \delta_{p0}$. We consider a simple energy band having a subsidiary minimum in $E(k)$ defined by the unperturbed problem. The equations defining the amplitudes $U(p)$ for the unperturbed problem are taken to be

$$0 = (-E + \epsilon_0) U(p) + \epsilon_1 [U(p+1) + U(p-1)] + \epsilon_2 [U(p+2) + U(p-2)], \quad p = \dots, -1, 0, 1, \dots \quad (1)$$

where $\epsilon_l = \int \phi(x) H_0(x) \phi(x-la) dx$. Only enough terms ϵ_l have been kept so that the subsidiary minimum can occur in $E(k)$. The solutions of this problem are

$$U(p) = e^{ikpa} \quad \text{and} \quad E(k) = \epsilon_0 + 2\epsilon_1 \cos k + 2\epsilon_2 \cos 2k. \quad (2)$$

If $\epsilon_1 > 0$ and $4\epsilon_2 < -\epsilon_1$, $E(k)$ exhibits a subsidiary minimum as shown in Figure 1.

The perturbed problem has solutions that are either symmetric, $U(p) = U(-p)$ or antisymmetric $U(p) = -U(-p)$, in p and because of the simple nature of the impurity energy V_{pq} it only affects the symmetric solutions. The equations for the perturbed problem are the same as for the unperturbed problem except for $p = 0, \pm 1$. By making use of the remaining unperturbed equations and the boundary condition that the wave function $U(p)$ must not become indefinitely large as p gets large we find that we may write $U(p) = Ae^{-\gamma p} + B \cos(kp - \alpha)$ for $p > 0$, when we are in the energy range Δ in Fig. 1, in which localized states associated with the subsidiary minimum

would be expected to occur. Here $k = k_1$ and $i\gamma = k_2$ are given, for E fixed, by the two solution for k of the dispersion relation, Eq. (2). The coefficients A and B are now determined by the homogeneous equations

$$\begin{aligned} U(1) - U(-1) &= 0, \\ V_0 U(0) + \varepsilon_2 [U(2) - U(-2)] &= 0, \end{aligned} \quad (3)$$

where in these equations $U(-p)$ means $U(p)$ for $p > 0$ evaluated formally for negative values of p . The existence of a localized solution requires $B = 0$, and it is easy to show that no such solutions exist in the energy range Δ .

Let us now consider a three-dimensional problem analogous to Slater and Koster's one-dimensional model. We consider an infinite three-dimensional crystal with one substitutional localized impurity. We assume that there is an energy band of the pure infinite crystal which is far from other bands and has a subsidiary minimum, and that there are no matrix elements of the impurity potential energy between states from different bands. The Schrodinger equation in the Wannier representation cannot be solved exactly in this case and it is more convenient to work with the "summation equation" form of the difference equations for the Wannier function amplitudes as derived by Slater and Koster. The summation equation is

$$U_i = \sum_{j \neq i} G_{ij} V_{j \neq i} U_j. \quad (4)$$

Here, $U_i (= U(\underline{R}_i))$ is the amplitude of the Wannier function centered at lattice point \underline{R}_i . $V_{ik} = \int \phi^*(\underline{r} - \underline{R}_i) V(\underline{r}) \phi(\underline{r} - \underline{R}_k) d^3r$ is the matrix element of the impurity potential energy between Wannier functions on sites \underline{R}_j and \underline{R}_k , and G_{ij} is the Green's function defined by the unperturbed

periodic potential problem:

$$G_{ij} = \frac{1}{N^3} \sum_{\substack{\underline{k} \text{ in} \\ \text{B.Z.}}} \frac{\exp[i\underline{k} \cdot (\underline{R}_i - \underline{R}_j)]}{E - E(\underline{k})} \approx \frac{1}{(2\pi)^3} \int_{\text{B.Z.}} \frac{\exp[i\underline{k} \cdot (\underline{R}_i - \underline{R}_j)]}{E - E(\underline{k})} d^3k, \quad (5)$$

where $E(\underline{k}) = \sum_m \epsilon_m e^{-i\underline{k} \cdot \underline{R}_m}$. We will now study a model which approximates our problem but for which analytic answers can be obtained. We consider a spherical band ($E(k)$ only where $k = |\underline{k}|$) and also consider the Brillouin zone to be spherical. A typical form for E might be $E(k) = \epsilon_1 \cos k + \epsilon_2 \cos 2k$ and $k_{\max} = \pi$ would be the radius of the zone. We keep two terms in $E(k)$ in order that there be a subsidiary minimum, and will evaluate the Green's function for an energy below the subsidiary minimum, but above the bottom of the band. Because we are only interested in a qualitative question, namely the admixture of continuum and bound components of states lying within an unperturbed energy band but below a subsidiary minimum, we may further approximate $E(k)$ by $E(k) = \alpha k^2 - \beta k^4$ where both α and β are greater than zero, thus ensuring the existence of a subsidiary minimum. We are particularly interested here in the case of the very localized impurity potential

$$V_{ij} = V_0 \delta(\underline{R}_i, 0) \delta(\underline{R}_j, 0). \quad (6)$$

In order to study this case we must have a finite value for G_{00} . In the case that no subsidiary minimum exists and $E(k)$ may be satisfactorily approximated by $E(k) = \alpha k^2$ it is necessary to treat seriously the existence of a high wave number cutoff (the Brillouin zone boundary) in the integral for G_{00} . Failure to do so leads to an infinite value for G_{00} . However, in the case we are treating such a cutoff is not

necessary to avoid a divergence of G_{00} , and for mathematical simplicity, we extend the range of the integration in \underline{k} space to include all of \underline{k} space. In this way we find

$$G_{ij}^0 \propto \int_{\text{all } \underline{k}} \frac{\exp[i \underline{k} \cdot (\underline{R}_i - \underline{R}_j)]}{E - 2\alpha k^2 + \beta k^4} d^3k$$

$$= [4\pi\beta(b^2 + c^2)]^{-1} \left\{ \frac{\cos b|\underline{R}_i - \underline{R}_j| - \exp[-c|\underline{R}_i - \underline{R}_j|]}{|\underline{R}_i - \underline{R}_j|} \right\}, \quad (7)$$

where b^2 and $-c^2$ are solutions of $E - 2\alpha k^2 + \beta k^4 = 0$. We may of course add to this result any solution of the homogeneous equation, i.e. the Schrodinger equation in the Wannier function representation for the periodic potential problem with energy E . We may usefully consider such solutions to be $e^{i \underline{k} \cdot (\underline{R}_i - \underline{R}_j)}$ where $E(\underline{k}) = E$. We thus consider Green's functions of the form

$$G_{ij} = G_{ij}^0 + K(\underline{k}) \exp[i \underline{k} \cdot (\underline{R}_i - \underline{R}_j)], \quad (8)$$

which give rise to solutions of a perturbed problem resembling as closely as possible unperturbed Bloch states. If the impurity potential is of the form (6) then the equation (5) gives rise to the eigenvalue condition

$$1 = V_0 G_{00}.$$

$$\text{or} \quad \frac{1}{V_0} = \frac{c}{4\pi\beta(b^2 + c^2)} + K(\underline{k}). \quad (9)$$

We see that for any energy that would give rise to a discrete level associated with the subsidiary minimum we may choose $K(\underline{k})$ to satisfy equation (9). Thus we see that no completely bound state can exist for

a very localized potential. Even if equation (9) could be solved with $K(k) = 0$, the resultant solution (for a single energy) would contain almost equal portions of localized and continuum parts. We have thus extended Slater and Koster's result for the absence of localized levels associated with a subsidiary minimum of an energy band and a strongly localized impurity potential to a three dimensional case.

Let us now for comparison examine the case of a Coulomb impurity potential screened by the static dielectric constant. The main point of our work is to show that this potential gives rise, for a spherical band, rigorously, in the limit that the potential is slowly varying, and approximately in other cases, to bound states which are coincident in energy with continuum states of the perturbed problem. For this purpose it is convenient to write the Schrodinger equation in the Bloch representation:

$$\sum_{\substack{n' \\ k'}} (n \underline{k} | H_0 + U | n' \underline{k}') A_{n'}(\underline{k}') d^3 k' = E A_n(\underline{k}). \quad (10)$$

Here $U(r) = e^2/\epsilon r$ (ϵ is the static dielectric constant) and $H_0 = (\hbar^2/2m) \nabla^2 + V(\underline{r})$ where $V(\underline{r})$ is the periodic potential. $U(r)$ is, of course, an approximate impurity potential energy which has been justified for semiconductors by many workers using recent many-body theory.³ Following Kohn⁴ we now write these equations in a form which separates the isolated band (subscript 0) under discussion from all other bands:

$$\begin{aligned}
(E_0(\underline{k}) - E) A_0(\underline{k}) + \sum_{\underline{k}'} (0 \underline{k} | U | 0 \underline{k}') A_0(\underline{k}') \\
+ \sum_{\substack{\underline{k}' \\ n' \neq 0}} (0 \underline{k} | U | n' \underline{k}') A_{n'}(\underline{k}') = 0, \\
(E_n(\underline{k}) - E) A_n(\underline{k}) + \sum_{\underline{k}'} (n \underline{k} | U | 0 \underline{k}') A_0(\underline{k}') \\
+ \sum_{\substack{\underline{k}' \\ n' \neq 0}} (n \underline{k} | U | n' \underline{k}') A_{n'}(\underline{k}') = 0, \quad n \neq 0,
\end{aligned} \tag{11}$$

where $A_n(\underline{k})$ is the amplitude of the Bloch function with wave vector \underline{k} in band n . Here we have used the fact that

$$(n \underline{k} | H_0 | n' \underline{k}') = E_n(\underline{k}) \delta_{nn'} \delta_{\underline{k} \underline{k}'}.$$

The matrix elements of the perturbation are given by

$$(n \underline{k} | U | n' \underline{k}') = \sum_{\underline{K}_v} C_{n \underline{k}; n' \underline{k}'}^v \left(\frac{-e^2}{2\pi\epsilon |\underline{K}_v + \underline{k}' - \underline{k}|^2} \right), \tag{12}$$

where \underline{K}_v is a reciprocal lattice vector and $C_{n \underline{k}; n' \underline{k}'}^v$ is the v th coefficient in the Fourier expansion of the product of the periodic parts of the Bloch functions $\psi_{n \underline{k}}(\underline{r})$ and $\psi_{n' \underline{k}'}(\underline{r})$. In particular $C_{n \underline{k}; n' \underline{k}'}^0 = \delta_{nn'}$.

The Coulomb potential is slowly varying except in the cell containing the impurity atom. In the familiar situation of a band with no subsidiary minimum it is assumed that only Bloch functions with wave vectors near the minimum will contribute appreciably to any bound impurity state wave functions. Thus all terms in Eq. (12) with $\underline{K}_v = 0$ are neglected, and all interband terms are at first neglected because the impurity potential matrix elements are much smaller than typical interband energies. Furthermore $E(\underline{k})$ is approximated by $E_0 + \frac{\alpha}{2} (\underline{k} - \underline{k}_0)^2$, an expression valid near

the band minimum \underline{k}_0 . The restriction that \underline{k} lie within the Brillouin zone is then lifted and the usual slowly varying hydrogen atom type envelope functions result, together with a hydrogen atom energy spectrum, for the bound levels. Finally one can check that the envelope functions only involve small \underline{k} values, thus establishing the consistency of the solution.

When a subsidiary minimum exists it is not clear that all $\underline{k}_v \neq 0$ can be neglected. Let us nevertheless make the same assumptions for the subsidiary minimum problem as were made in the case in which there is only an absolute minimum and examine the justification later. We neglect all $\underline{k}_v \neq 0$, and interband effects, and we extend the range of \underline{k} out of the Brillouin zone into all reciprocal space. However we now use an $E(\underline{k})$ that allows a subsidiary minimum. In addition we assume a spherical band in order that we can solve the equations for the envelope function. The impurity equation in \underline{k} space then becomes

$$(E(\underline{k}) - E) A_0(\underline{k}) + \frac{1}{2\pi} \int \frac{e^2}{|\underline{k} - \underline{k}'|^2} A_0(\underline{k}') d^3k' = 0, \quad (13)$$

where the sum over \underline{k}' in (11) has been changed to an integral.

We take $E(\underline{k}) = \epsilon_0 + \epsilon_1 \cos k + \epsilon_2 \cos 2k$ where the conditions $\epsilon_1 + 4\epsilon_2 < 0$ and $\epsilon_1 > 0$ establish a subsidiary minimum at $\underline{k} = 0$ and an absolute minimum at $\underline{k} = \pi$. Here k is the magnitude of \underline{k} .

If we now return the problem to "real" space by multiplying by $e^{i\mathbf{k} \cdot \mathbf{r}}$ and integrating over reciprocal space, we find the following equation for the envelope function $x(\underline{r})$

$$[\cos([- \nabla^2]^{\frac{1}{2}}) + \delta \cos(2[- \nabla^2]^{\frac{1}{2}}) - \eta/\eta] \chi(\underline{r}) = -\epsilon \chi(\underline{r}) \quad (14)$$

where $\delta = \epsilon_2/\epsilon_1$, $\eta = e^2/\epsilon\epsilon_1$, and $\epsilon = (E - \epsilon_0)/\epsilon_1$. Here we understand the cos terms to mean their power series. Because the Hamiltonian is spherically symmetric we can write

$$\chi(r) = R(r) Y_l^m(\theta, \phi).$$

We then find that

$$\nabla^2 \chi = \left[O_r R - \frac{l(l+1)}{r^2} R \right] Y_l^m(\theta, \phi),$$

where

$$O_r = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right).$$

Similarly,

$$(\nabla^2)^n \chi = \left(O_r - \frac{l(l+1)}{r^2} \right)^n R(r) Y_l^m(\theta, \phi).$$

Let us first treat the case $l = 0$. We let $R(r) = F(r)/r$ and find that the equation for F becomes

$$\sum_{n=0}^{\infty} \frac{F^{2n}}{(2n)!} + \delta \sum_{n=0}^{\infty} \frac{2^{2n} F^{2n}}{(2n)!} - \frac{\eta}{r} F = -\epsilon F, \quad (15)$$

where $F^{2n} = \frac{d^{2n} F}{dr^{2n}}.$

This equation is a generalization of the confluent hypergeometric equation⁵, and it is thus not surprising that when we try a solution of the form $R(r) = e^{-\alpha r}$ the resulting equations for α ,

$$\cosh \alpha + \delta \cosh 2\alpha + \epsilon = 0, \quad (a)$$

$$-\sinh \alpha - 2\delta \sinh 2\alpha - \eta = 0, \quad (b) \quad (16)$$

have a solution with α real. These equations arise when the coefficients of the different powers of r are set equal to zero. Eq. 16 (a) gives the energy when α is known and Eq. 16 (b) gives α in terms of the parameters of the problem, including the strength of the impurity potential. Equation 16 (b) has two solutions for α , one real and positive, and the other of the form $\alpha = i\pi + \gamma$, where γ is positive. These solutions correspond to bound states splitting off from the band at $\underline{k} = 0$ and $\underline{k} = \pi$ respectively.

For α or γ small the equations may be solved approximately yielding the usual effective mass results:

$$\alpha = -\frac{\eta}{1+4\delta}, \quad \epsilon_{\alpha} = -\delta - 1 + \frac{\eta^2}{2|1+4\delta|};$$

$$\gamma = \frac{-\eta}{-1+4\delta}, \quad \epsilon_{\gamma} = -\delta + 1 + \frac{\eta^2}{2|1+4\delta|}. \quad (17)$$

It can be seen that for the form of $E(k)$ that we used $\alpha > \gamma$ no matter what the values of η and δ but that equality of these quantities is approached when δ becomes large. Bound states of higher energy for $\ell = 0$ can undoubtedly be constructed. For $\ell \neq 0$ it is not possible to solve the differential equation exactly. However, for large r all contributions from $\ell(\ell+1)/r^2$ in Equation 14 are negligible so that the asymptotic solution $e^{-\alpha r}$, where α has a positive real part is again possible.

Our result shows that, to the extent that the potential energy in the equation for the envelope function can be assumed to be Coulomb-like, bound impurity states of the effective mass type may be associated with a subsidiary minimum in a spherical band. In contrast with the case of

the very localized impurity, it is not true that all states with energies in the unperturbed band region contain admixtures of continuum states. It is reasonable to expect that this result does not depend critically on the use of a spherical band but we have not studied this point in detail.

Of great interest is the possible effect of a deviation of the potential that should be inserted in the envelope equation from the Coulomb form. In this connection we remember that there are two effects to consider: the neglect of $K_v \neq 0$ and the extension of the Brillouin zone to all of \underline{k} space. These effects are indeed connected. Consider first the effect of the extension of the band to all reciprocal space on the term $1/|\underline{k} - \underline{k}'|^2$. If the band were not extended we would be omitting high $\underline{k} - \underline{k}'$, thus putting a bottom on the potential well. This should not matter as long as no bound states lie near the bottom of the well. Now consider the term proportional to $1/|\underline{k} - \underline{k}' - K_v|^2$. The coefficient of this term, $C_{\underline{0}\underline{k};\underline{0}\underline{k}'}^v$, is not likely to be greater than unity but can be counted on to be of order unity until v gets large, in which case no large contributions are expected anyway. We will neglect the \underline{k} and \underline{k}' dependences of $C_{\underline{0}\underline{k};\underline{0}\underline{k}'}^v$ and set this coefficient equal to unity. We are thus led to terms in the potential energy of the form

$$\int_{B.Z.} \frac{\exp[i(\underline{k} - \underline{k}') \cdot \underline{r}_m]}{|\underline{k} - \underline{k}' - K_v|^2} d^3 k. \quad (18)$$

If we extend the boundary of the Brillouin zone to infinity this term gives

$$e^{i\vec{K}_\nu \cdot \vec{r}} \int \frac{\exp[i(\vec{k} - \vec{k}' - \vec{K}_\nu) \cdot \vec{r}]}{|\vec{k} - \vec{k}' + \vec{K}_\nu|^2} d^3(\vec{k} - \vec{k}' - \vec{K}_\nu)$$

$$\propto \frac{e^{i\vec{K}_\nu \cdot \vec{r}}}{r}$$

Including both \vec{K}_ν and $-\vec{K}_\nu$, we get a contribution to the potential of the form

$$V \propto \frac{\cos \vec{K}_\nu \cdot \vec{r}}{r} \quad (19)$$

Terms such as Eq. (19) are smaller than the $1/r$ we have been using. If the zone is not extended to infinity, the integrals become very hard to do, and it is questionable whether the approximations of the problem warrant such a calculation. This discussion shows that it is not easy to find the proper potential to use in the envelope function equation when the real potential (for low lying states) in the Schrodinger equation is the Coulomb potential. However, it is also indicated that the Coulomb potential is surely of the right order of magnitude and it is a bit surprising that bound states coincident in energy with continuum states exist for this potential. Perhaps there is a mathematical connection with the fact that the Klein-Gordon equation, in which the kinetic energy can also be thought of as a series in powers of the Laplacian operator, has bound solutions for the hydrogen atom.

A change in the potential from the Coulomb form will probably change the wave functions enough to cause bound states coincident in energy with

continuum states to no longer be eigenstates of the impurity problem, but if so the lifetimes of these states will probably be long. An estimate was made of the lifetime of a bound state of the form $u_0(\underline{r})e^{-\alpha r}$ with respect to decay into continuum states of the same energy, using a potential of the form (19) summed over the smallest reciprocal lattice vectors and a spherical band of the form used above. The result for the width ΔE of the bound state is

$$\Delta E \cong 3^{(1/2)} 4^{-2} 5^{-3} \pi^{-2} (B\mathcal{B})^2 \left(\frac{e^2 \alpha}{2\epsilon} \right) (\alpha a) \left[\frac{e^2 \alpha}{2\epsilon} \frac{1}{|2\epsilon_2 - \epsilon_1|} \right]^{(20)}$$

where B and \mathcal{B} arise from expansions of products of the periodic parts of two Bloch functions from the same band in terms of a Fourier series in reciprocal lattice vectors,⁶ and are of order of unity; a is the Bohr radius, and all other symbols have been defined earlier. Here $e^2 \alpha / 2\epsilon$ is the energy of a shallow impurity and we see that ΔE is smaller than this by two factors, the first being the ratio of the impurity energy to an energy of the order of a band width, and the second the ratio of the Bohr radius to the impurity orbit radius. Eq. (20) gives a lifetime for a typical shallow impurity of 10^{-8} -- 10^{-9} sec.

In summary, we may say that impurity levels with very long lifetimes are associated with subsidiary minima for a Coulomb impurity potential, although no such levels exist for a very localized impurity potential. It would be interesting to know how slowly the impurity potential must vary in order that localized impurity levels be associated with subsidiary minima.

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 5. All solutions of equation 15 can be found by making a Laplace transform.
 6. See Equation 12 and the discussion following it.

Figure Captions.

Figure 1. $E(k)$ for an energy band having a subsidiary minimum at $k = 0$.

